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ORIGINAL ARTICLE

Assessing medicinal qualities of groundwater from the Busko-Zdrój area (Poland) using the probabilistic method

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Abstract In Poland, curative waters, as minerals, are a subject to the Geological and Mining Law (GML in Geological and mining law of 9 June 2011 (Journal of Laws [Dz. U.] No. 163/2011 item 981), 2011). In accordance with the guidelines set forth in this Law, as a curative waters are recognised groundwaters uncontaminated by chemical and microbiological agents, which should exhibit a natural variability of physicochemical parameters and fulfil at least one of the conditions listed in the Law concerning minimum concentrations of the specific components that determine the medicinal properties of waters. Pursuant to the *Regulation of the Minister of Health* (RMH in Regulation of the Minister of Health of 13 April 2006 on the scope of the studies required to determine the medicinal properties of natural medicinal resources and medicinal properties of climate, the criteria for their evaluation and a specimen certificate confirming these properties (Journal of Laws [Dz. U.] No. 80/2006 item 565), 2006), the assessment of medicinal properties of groundwaters is based on documented studies that must span 3 years at the minimum. In this paper, the assessment of medicinal qualities of the waters occurring in the Busko-Zdrój area (Poland) using the deterministic method and three variants of the probabilistic method is presented.

Keywords Mineral waters · Curative waters · Medicinal qualities · Measurement uncertainty · Poland

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Introduction

In European Union law, there are no regulations directly applicable to curative waters. These waters are subject to the general requirements contained in Directive 2001/83/EC *of the European Parliament and of the Council of 6 November 2001 on the Community code relating to medicinal products for human use* (Directive 2001) as amended by Directive 2004/27/EC of 31 March 2004 (Directive 2004). The Directives neither provide any definition of curative waters nor specify any parameters that determine their medicinal qualities.

In Poland, curative waters, as minerals, are a subject to the *Geological and Mining Law* of 9 June 2011 (Journal of Laws [Dz.U.] No. 163/2011 item 981—GML 2011). In accordance with the guidelines set forth in this Law, curative waters are recognised groundwaters uncontaminated by chemical and microbiological agents, which should exhibit a natural variability of physicochemical parameters and meet at least one of the conditions listed in the Law concerning minimum concentrations of the specific components that determine the medicinal properties of waters (Table 1). Pursuant to the *Regulation of the Minister of Health of 13 April 2006 on the scope of the studies required to determine the medicinal properties of natural medicinal resources and medicinal properties of climate, the criteria for their evaluation and a specimen certificate confirming these properties* (Journal of Laws [Dz.U.] No. 80/2006 item 565—RMH 2006), the assessment of medicinal properties of groundwaters is based on documented studies that must span 3 years at the minimum.

This assessment can be conducted using the deterministic or probabilistic methods (Fig. 1). In the deterministic method, the individual results of analysis of specific parameters in water samples or the mean values of

Table 1 Criteria for assessing medicinal properties of groundwaters—a comparison of the guidelines contained in (RMH 2006) and (GML 2011)

Component	Threshold value	
	GML (2011)	RMH (2006)
Mineralisation	1000 mg/L	1000 mg/L
Major ions		
Chloride ions	–	20 % mval
Sulphate ions	–	
Bicarbonate ions	–	
Sodium ions	–	
Calcium ions	–	
Magnesium ions	–	
Specific components		
Fluoride ions	2 mg/L	2 mg/L
	Water containing fluoride	
Iodide ions	1 mg/L	1 mg/L
	Water containing iodide	
Iron (II) ions	10 mg/L	10 mg/L
	Ferruginous water	
Metasilicic acid	70 mg/L	70 mg/L
	Water containing silica	
Free carbon dioxide	250–999 mg/L	250–999 mg/L
	Water containing	Water containing
	Carbon dioxide	Carbon dioxide
	1000 mg/L	1000 mg/L
	Carbonated water	Carbonated water
Sulphur (II) compounds	1 mg/L	1 mg/L
	Sulphurous water	
Radon	74 Bq/L	74 Bq/L
	Radon water	
Temperature	20 °C	20 °C
	Thermal water	

measurements for multiple samples taken from the intake, are compared against the threshold values set forth in applicable legislation. The decision about medicinal character of water is made only on the basis of the obtained results, and any errors related to sampling and analysis (both systematic and random) are not included. This suggests that measurement uncertainty is zero (Demetriades 2010).

In the probabilistic approach, the methodology described by Ciężkowski (2007) may be applied, whereby the mean concentrations of specific components minus two standard deviations are compared against threshold values, or the methodology proposed by Wątor (2013), which is based on publications (Ellison and Williams 2007; ISO 2006b, 2008; Kmiecik 2011) and includes the information on measurement uncertainty in the assessment of medicinal qualities of waters. In this situation the acceptable level of probability of making a wrong decision is considered, and proper decision rules should be defined. An acceptance zone and a rejection zone must be estimated (Witczak et al. 2006; Ellison and Williams 2007; Demetriades 2010). When measured concentration of considered specific component lies in acceptance zone, then we can recognise analysed water as specific curative water. In opposite situation, when the analysed concentrations of the specific components are in the rejection zone, then considered waters cannot be assessed as curative. The use of the uncertainty allows to include not only effects associated with the results dispersion (random error as in the case when only standard deviation from multiple results is taken into account) but also some systematic errors. Furthermore, the use of the measurement uncertainty gives the possibility to implement the probabilistic method in the assessing medicinal qualities of water also for the individual results.

Identifying and calculating the uncertainty concerning with the determination of chemical components is an important element of the measures related to groundwater monitoring, also with respect to assessing medicinal qualities of water. Both single-test results and the mean value used in the decision making process involve uncertainty that is inherent in the process of groundwater quality assessment.

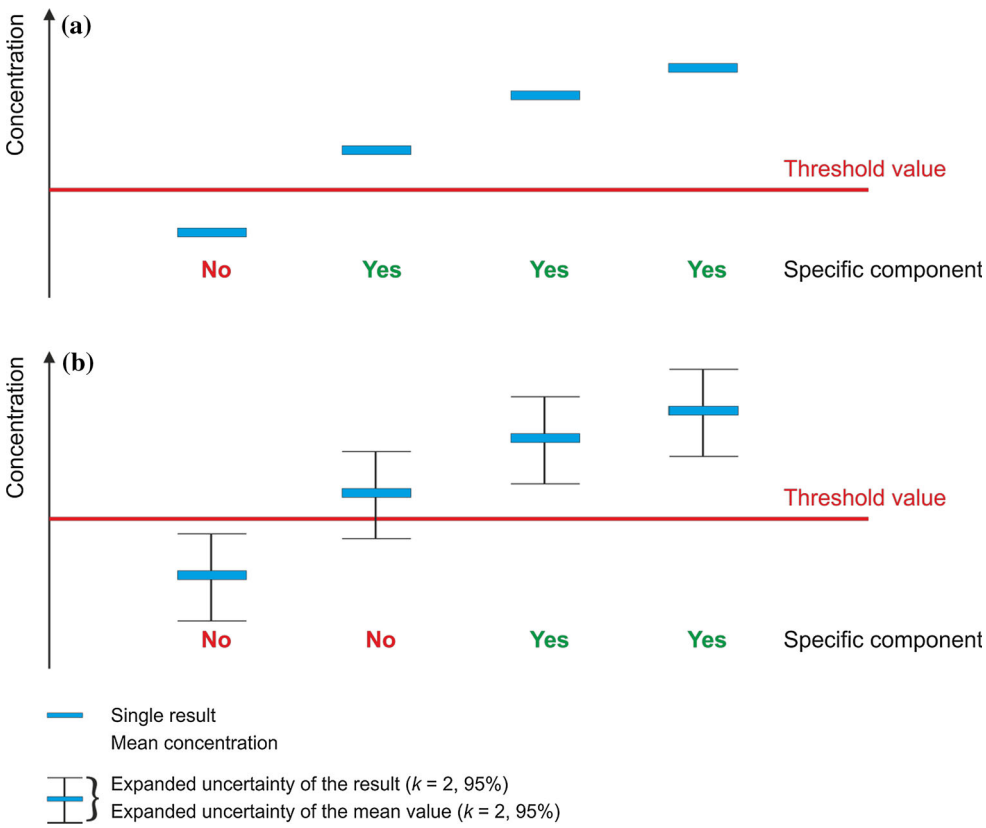

Fig. 1 Assessing medicinal qualities of water using **a** the deterministic method; **b** the probabilistic method

In Poland, curative and geothermal water are very wide used in spas for medical treatment in baths and swimming pools, drinking treatment (crenotherapy), inhalation, irrigation, and rinsing (Chowaniec and Zuber 2008; Ciężkowski et al. 2010; Dowgiałło 2012; Górecki et al. 2014; Hałaj 2014; Tomaszewska and Szczepański 2014; Tomaszewska et al. 2014). In various publications the effects of different types of thermo-mineral and geothermal waters used in spas in treatment purposes were studied (Cruz and Franca 2006; Lambrakis et al. 2012; Balderer et al. 2014; Karagülle and Karagülle 2015; Tenti et al. 2015). Some of them presents also the results of investigation to use in balneotherapy the combine the therapeutic effects of clays and mineral waters, known as pelotherapy (Gámiz et al. 2009; Rebelo et al. 2011, 2014).

In this paper, an assessment of medicinal qualities of the waters occurring in the Busko-Zdrój area (Poland) is carried out. The deterministic method and three variants of the probabilistic method are presented.

Study area

The study concerned curative waters from the intakes located in Busko-Zdrój. Busko-Zdrój is a town in the Świętokrzyskie Province, the Busko district, in the municipality of Busko-Zdrój. It lies approximately 80 km from Kraków and 230 km from Warszawa (Fig. 2).

An important factor affecting the hydrogeological conditions in the Busko area is dislocation occurring in the form of a reverse fault, oriented NW–SE (Barbacki 2007). Two types of curative water occur here. The first one is associated with deep circulation system (from Jurassic marls and limestones) and provides saline water containing high concentration of chlorides, sodium ions, iodides, iron (II) ions, and fluorides. The second is connected with shallow circulation system and include, *inter alia*, chloride-sodium, sulphide, and iodide waters (Cl–Na, H_2S, I), mostly associated with Cretaceous formations (marls and limestones of Santonian and sandstones of Cenomanian). They usually occur under Miocene gypsums and clays (Fig. 3). Due to the high hydrostatic pressure these are the artesian or subartesian waters with temperature range from 12 to 14 °C (Porwisz and Madry 2000). Waters from the following Cretaceous intakes in Busko-Zdrój have been analysed: B-4b Aleksander, B-8b Michał, B-13 Anna, B-16a Wiesława, and B-17 Ignacy (Table 2; Fig. 2).

The assessment of medicinal water characteristics was performed on the basis of the results obtained during last 10 years (from 2005 to 2014). Basic information about intakes and values of the parameters measured in the field

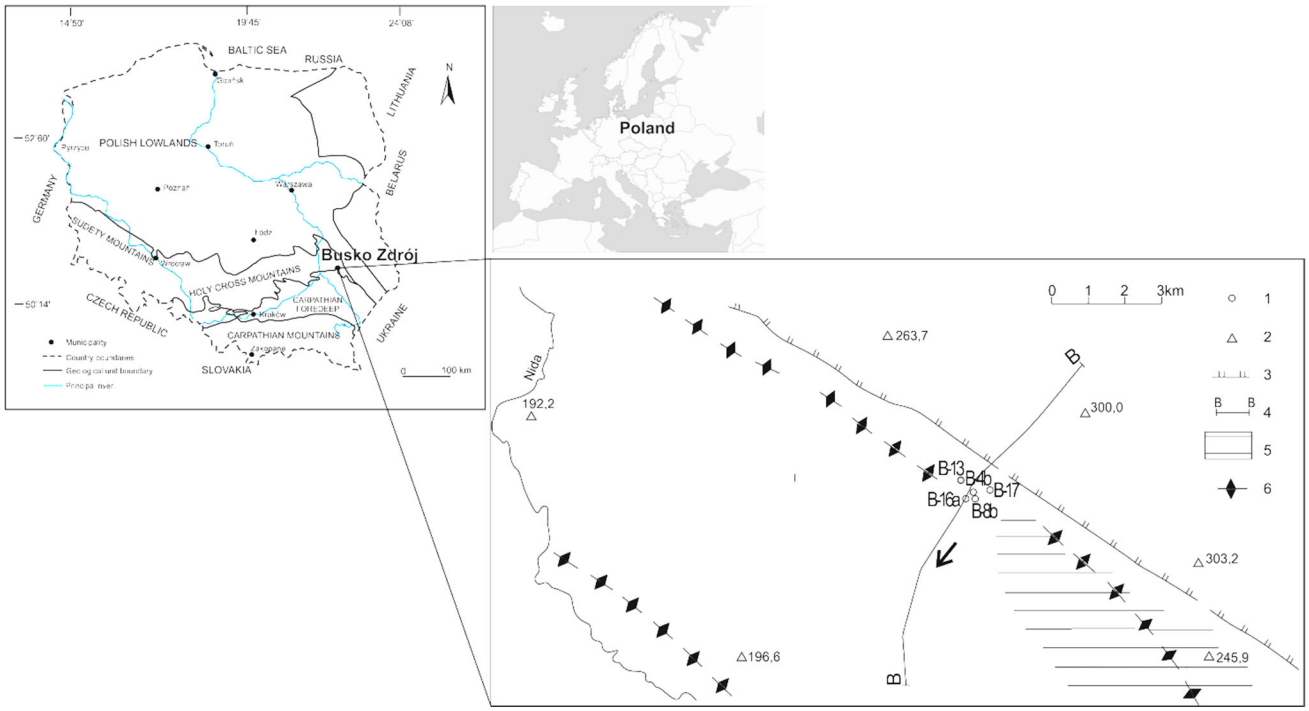

Fig. 2 Location of Busko-Zdrój and study area (based on Krawczyk et al. 1999). Explanations: *1* boreholes with curative waters, *2* head points [m a.s.l.], *3* fault zone of Radzanów in Jurassic formations, *4* geological cross section, *5* area reach without Cenomanian formations, *6* morphological axes of elevations of Jurassic

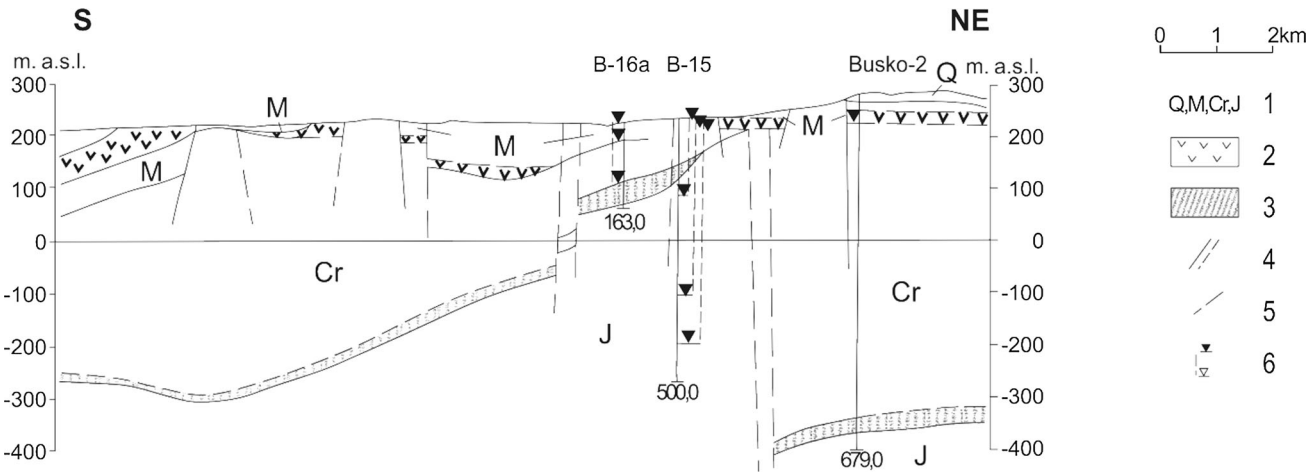

Fig. 3 Hydrogeological cross-sectional sketch (Krawczyk et al. 1999). Explanations: *1* stratigraphic (*Q* Quaternary, *M* Miocene, *Cr* Cretaceous, *J* Jurassic), *2* gypsum and anhydrites, *3* Cenomanian sands and sandstones, *4* faults, *5* landscape photolineaments, *6* mineral water table

are shown in Table 2. Chemical characteristics of these waters are compiled in Table 3 and Fig. 4.

In analysed waters, sodium ions are the dominate cations and chlorides, respectively, are the dominate anions. Mineralisation of water in described intakes varies from 11 to 16 mg/L. Waters include also some specific parameters, like sulphur (II) compounds and iodide ions. For these reasons, they are named as mineral specific waters chloride-sodium, sulphides, and iodides. Chemical characteristics of analysed waters are compiled in Table 3 and presented in Fig. 4. Kurlov's formula is the best known and frequently used method for expressing the chemical composition of water. It is a fraction with anions in its numerator and cation in its denominator. The ions are presented according to decreasing contents, the concentration data (mg/L) being written in the form of a subscript.

Table 2 Basic characteristics of the analysed intakes

Intake name (location on Fig. 2)	GPS coordinates		Depth (m)	Ordinate land (m a.s.l)	Aquifer		Parameter measured in the field (range for 2005–2015 years)	
	Latitude	Longitude			Lithology	Stratigraphy[a]	pH	γ_{25} (mS/cm)
B-4b Aleksander	N50°27.315′	E20°43.142′	55.0	217.7	Marls	Cr_s	6.72–7.45	20.40–21.50
B-8b Michał	N50°27.377′	E20°43.079′	60.0	217.8	Marls	Cr_s	6.99–7.53	19.44–20.80
B-13 Anna	N50°27.520′	E20°42.811′	55.0	219.7	Marls	Cr_s	7.01–7.48	18.47–19.52
B-16a Wiesława	N50°27.265′	E20°42.908′	163.0	215.0	Sandstones	Cr_c	6.92–7.55	19.83–20.80
B-17 Ignacy	N50°27.282′	E20°43.400′	148.0	219.9	Sandstones	Cr_c	6.96–7.30	20.50–21.80

[a] Cr_s—Cretaceous, Santonian; Cr_c—Cretaceous, Cenomanian

Table 3 Chemical characteristics of waters from the intakes tested

Intake name (location on Fig. 2)	Chemical composition according to Kurlov's formula I, F, Fe, H_2S (mg/L) M (g/L) (year of analysis)	Type of water according to RMH (2006)	Type of curative water
B-4b Aleksander	$I^{2.4}F^{0.6}H_2S^{28.6}$ $M_{13.8}\frac{Cl^{81}SO_4^{14}}{Na^{80}}T^{12.2}$ (2010)	1.40 % Cl–Na, H_2S, I	Sulphide and iodide water
B-8b Michał	$I^{1.9}F^{1.2}H_2S^{45.2}$ $M_{13.2}\frac{Cl^{79}SO_4^{17}}{Na^{81}}T^{12.4}$ (2002)	1.32 % Cl–Na, H_2S, I	Sulphide and iodide water
B-13 Anna	$I^{1.7}F^{0.9}H_2S^{40.4}$ $M_{12.4}\frac{Cl^{79}SO_4^{17}}{Na^{80}}T^{11.2}$ (2000)	1.24 % Cl–Na, H_2S, I	Sulphide and iodide water
B-16a Wiesława	$I^{1.9}F^{1.1}H_2S^{35.9}$ $M_{13.9}\frac{Cl^{80}SO_4^{17}}{Na^{79}}T^{15.9}$ (1999)	1.39 % Cl–Na, H_2S, I	Sulphide and iodide water
B-17 Ignacy	$I^{2.0}F^{1.1}H_2S^{53.2}$ $M_{14.3}\frac{Cl^{78}SO_4^{19}}{Na^{80}}T^{12.2}$ (2003)	1.43 % Cl–Na, H_2S, I	Sulphide and iodide water

To the left of the fraction, total mineralisation *M* (mg/L) is presented together with the contents of predominating gases (mg/L) and temperature *T* (°C) on the right (Tölgyessy 1993).

Methodology

The assessment of medicinal qualities of the waters was based on the results of analyses of their specific components (sulphides and iodides) performed from 2005 to 2014 for the intakes sourcing groundwater from the Cretaceous level—B-4b Aleksander, B-8b Michał, B-13 Anna, B-16a Wiesława and B-17 Ignacy (Fig. 2).

Water samples from the intakes were taken in accordance with the guidelines contained in Polish Standard PN-ISO 5667-11:2004 (ISO 2004), the Guidebook of selected physical and chemical groundwater contamination indicators and methods for their determination (Witczak et al. 2013) and the practical guidelines described by Zdechlik et al. (2013). All samples were collected by the same person with the use of the same sampling protocol (manual sampling). Single samples were taken to the appropriate bottles, filtrated in the field, and preserved according to the methods of analysis. The researches provide by Kmiecik and Podgórni (2009) indicates that the change of sampler has a significant influence on the uncertainty associated with sampling and on the measurement uncertainty too. When one person collects samples using one sampling protocol, only random effects are included in the uncertainty. In this situation statistical errors should also be estimated.

In 2011 and 2012, along with the normal samples, the sampler also collected control duplicate samples, which served to estimate measurement uncertainty according to the methodology described in Kmiecik (2011). In total, 19 pairs of normal and duplicate samples were collected for the determination of iodide ion concentrations and 12 pairs

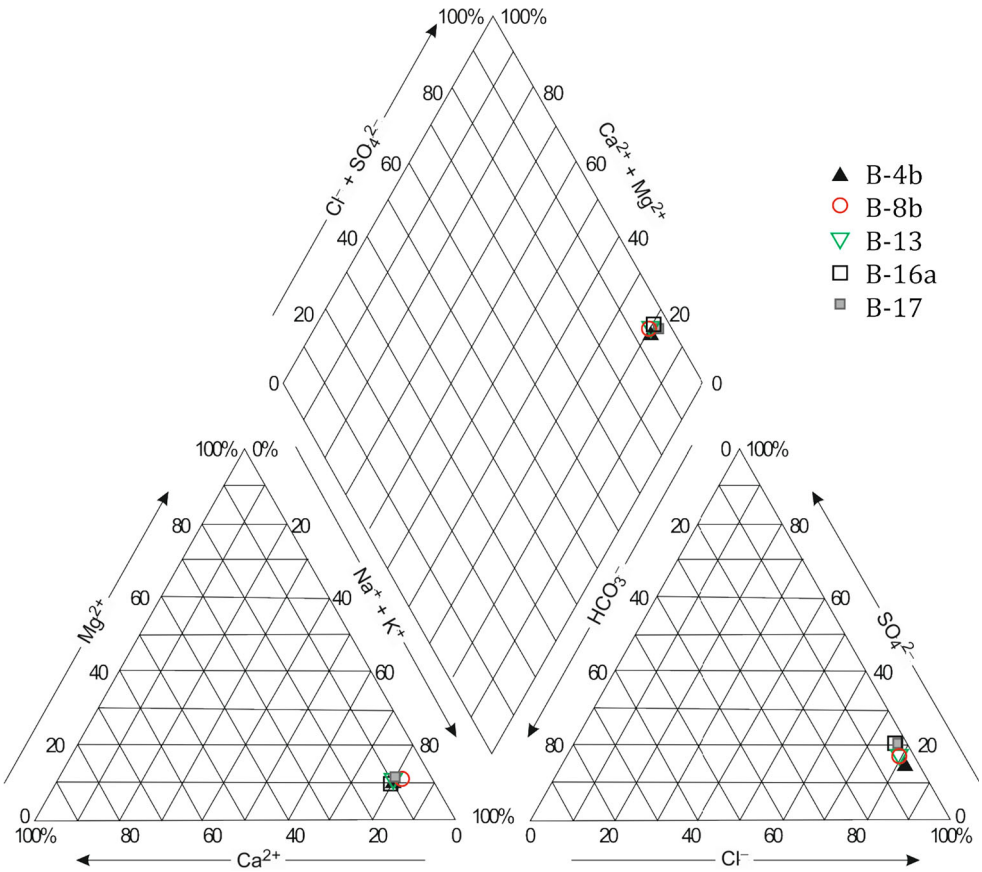

Fig. 4 Piper diagram for the analysed waters

Table 4 Characteristics of methods used for the determination of specific components of the curative waters analysed

Laboratory	Component	Analytical method	No of standard/procedure	Limit of determination (mg/L)	U_{lab} (%)[a]	$U_{measurement}$ (%)[b]
AB 176	Sulphur (II) compounds	Titration (thiomercurimetric)	Polish Standard PN–82/C–04566/03 (ISO 1982)	0.04	20.0	9.7
AB 1050	Iodide ions	Inductively coupled plasma mass spectrometry (ICP-MS)	Procedure PB–01, 2010 (based on standards (ISO 2007) and (ISO 2006a))	0.01	24.7	12.2

[a] The relative measurement uncertainty declared by the laboratory (95 % probability level)

[b] Uncertainty estimated on the basis of duplicate control samples (ROBAN programme)

of samples for the determination of sulphur (II) compounds.

Specific components were analysed at accredited laboratories: Hydrogeochemical Laboratory at the Department of Hydrogeology and Engineering Geology of the AGH University of Science and Technology in Krakow (Certificate of Accreditation No. AB 1050) for the determination of iodide ions; and the Laboratory of the Provincial Environmental Protection Inspectorate in Kraków (AB 176) for the determination of sulphur (II) compounds. These laboratories use the reference methods recommended for testing the chemical composition of groundwaters (Rice et al. 2012; Witczak et al. 2013), which have been validated for the determination of selected medicinal water components. Basic parameters of these methods are summarised in Table 4.

The relative expanded uncertainties declared by the laboratories are higher than these estimated on the basis of the results of analyses for duplicate samples. This results from the fact that in uncertainty estimating process, the laboratories took into account also the systematic errors (bias) resulting from changing the sampler or analyst.

The method of duplicate control samples is the simplest and probably the most cost-effective empirical method

Table 5 Summary of analysis results

Intake name	Number of data	Mean value (mg/L)	Standard deviation (mg/L)	Minimum (mg/L)	Maximum (mg/L)
Sulphur (II) compounds					
B-4b Aleksander	18	23.76	3.89	18.00	31.36
B-8b Michał	18	38.33	5.22	31.00	46.40
B-13 Anna	18	43.29	7.26	34.00	59.20
B-16a Wiesława	18	39.10	8.58	19.89	55.20
B-17 Ignacy	18	47.58	10.70	29.68	67.20
Iodide ions					
B-4b Aleksander	18	1.57	0.59	0.57	2.43
B-8b Michał	18	1.52	0.94	0.33	3.57
B-13 Anna	18	1.53	0.98	0.34	3.20
B-16a Wiesława	18	1.78	1.43	0.58	6.04
B-17 Ignacy	18	1.66	0.77	0.60	2.89

used for uncertainty estimation. It should be noted, however, that the duplicate sample method does not include sampling bias, which should be assessed separately, using, e.g. several samplers and several sampling procedures and/or interlaboratory sampling comparisons. However, this method of estimating uncertainty can be applied to minimise the bias, i.e. opting for the sampling to be performed by a single sampler, using the same sampling procedure and performed analysis in a single laboratory by a single analyst using the same analytical method. Full description of five different empirical methods for the estimation of measurement uncertainty is presented in publication: Ramsey and Ellison 2007; Demetriades 2010.

The determination of sulphur (II) compounds in water is difficult. In contact with air, they oxidise easily and quickly, and therefore it is advisable to perform analysis in the field immediately after collecting the sample. When samples are transported to a laboratory, suitable substances to preserve them should be used. Samples also must be collected without admitting air. It is necessary to remember, however, that these results will exhibit poorer precision and accuracy (Witczak et al. 2013). The thiomercurimetric methods used for sulphur (II) compound determination is one of the titration methods. Samples collected should be preserved by the sodium edetate addition. Analysed sample is titrated with the solution of the *o*-hydroxymercurybenzoic acid salt in the presence of dithizone as an indicator.

The determination of iodide concentrations in test samples is also difficult owing to the high levels of chloride ions. In these circumstances, using methods that involve ion-selective electrodes or even ion chromatography is not possible because interference is too large and the results obtained exhibit insufficient accuracy and precision. The use of inductively coupled plasma mass spectrometry (ICP-MS) for iodine determination gives possibility to avoid some adverse matrix effects and interferences. The very important thing is to collect representative samples. Because iodine compounds are usually volatile and unstable, it is necessary to storage samples in dark bottles without contact with air.

Data analysis: assessing the medicinal qualities of waters

Table 5 summarises the main descriptive statistics concerning analysis results for individual intakes.

On the basis of the results of specific components analyses obtained, the medicinal qualities of the groundwater intakes have been assessed using the deterministic and probabilistic methods.

In the deterministic method, the mean value of the parameter analysed for the water from the intake is directly compared to the threshold value. If the result is below the required threshold value, the parameter analysed cannot be considered a specific component of the water. If the result is higher than the threshold value, the parameter can be taken into account in the description of the hydrogeochemical characteristics of water.

In the probabilistic method, three assessment variants have been used: In the first variant, the mean value less two standard deviations ($\bar{x}-2\sigma$) was compared to the threshold value according to the methodology recommended by Ciężkowski (2007), and in subsequent two variants the mean value minus the uncertainty of the mean value ($\bar{x} - U_{\text{mean}}$) was used [according to the methodology proposed by Wątor (2013)] (Table 4). The uncertainty declared by the laboratory was taken into account:

Table 6 Comparison of analysis results to threshold values for specific components in waters from Cretaceous level intakes, deterministic method

Compound	Threshold value according to RMH (2006) and GML (2011)	Intake name				
		B-4b Aleksander Mean value	B-8b Michał	B-13 Anna	B-16a Wiesława	B-17 Ignacy
Sulphur (II) compounds (mg/L)	1	23.76	38.33	43.29	39.10	47.58
Iodide ions (mg/L)	1	1.57	1.52	1.53	1.78	1.66
Hydrogeochemical type of water due to the content of specific components		Sulphide and iodide water	Sulphide and iodide water	Sulphide and iodide water	Sulphide and iodide water	Sulphide and iodide water

$$U_{\text{mean\_lab}} = \frac{U_{\text{lab}}}{\sqrt{n}}$$

and also the uncertainty estimated empirically on the basis of duplicate control samples in accordance with the guidelines provided in Kmiecik (2011) and based on publications (Ramsey et al. 1992; Ramsey 1998, 2009; Ramsey and Argyraki 1997; Ellison et al. 2000; Ellison and Williams 2007; Ramsey and Ellison 2007):

$$U_{\text{mean}} = \frac{U_{\text{measurement}}}{\sqrt{n}}$$

where U_{lab}—determination uncertainty value declared by the laboratory (taking into account the uncertainty associated with the collection of samples), $U_{\text{measurement}}$—measurement uncertainty value estimated using the ROBAN[1] programme on the basis of duplicate control samples, and n—the number of samples.

Probabilistic approach in compliance assessment is mostly important when analysis results are close to the threshold values that determine, e.g. the medicinal qualities of the water (Kmiecik 2011). However, in order to use the probabilistic method, it is necessary to specify the appropriate decision rules (Ellison and Williams 2007) that enable the determination whether the threshold value has been reached or not.

In this paper, the rule is defined as follows: A parameter can be considered a specific component resulting in medicinal qualities of the water from the analysed intakes, when the average value determined minus the amount of uncertainty or minus two standard deviations is above the applicable threshold value. The considered level is thus *the concentration of a specific component at which we can state with a confidence level of 95 % that the threshold value has been reached* (Fig. 1).

[1] ROBAN computer program bases on the analysis of variance. Apart from classical ANOVA it has also implemented the robust ANOVA algorithm (rANOVA). The robust method is used when the outliers occur in the analysed data set. Further information is described in publications: Ramsey et al. (1992), Ramsey (1998), Lee and Ramsey (2001), Roban (2001), Witczak et al. (2006), Lyn et al. (2007) and Demetriades (2010).

Deterministic method

When analysing mean determination values for the specific components present in the tested waters from the Cretaceous level, it can be seen that both the average concentrations of sulphur (II) compounds (H_2S) and iodide ions (I^-) are above threshold values (Table 6; Fig. 5).

On this basis, waters from intakes B-4b, B-8b, B-13, B-16a and B-17 should be considered specific mineral waters (sulphide and iodide ones).

Probabilistic method

Results of assessment of medicinal qualities of waters using the probabilistic method are summarised in Table 7 and in Fig. 6.

In accordance with the above-defined decision rule (the decision threshold is the concentration of a specific component for which we can state with a confidence level of 95 % that the threshold value has been reached), for sulphur (II) compounds in the analysed Cretaceous level water intakes, the threshold value has been reached (irrespective of the probabilistic method used), as the lower bounds of variation/uncertainty intervals lie well above the threshold values set forth in applicable current legislation (Table 7; Fig. 6).

In the case of iodide ions, for all the intakes analysed mean values less than two standard deviations lie below the required threshold value. In this case, these cannot be considered specific components of these waters and should not be included in their characteristics (Table 7; Fig. 6). Therefore, the waters from the intakes analysed should be considered as only sulphide waters.

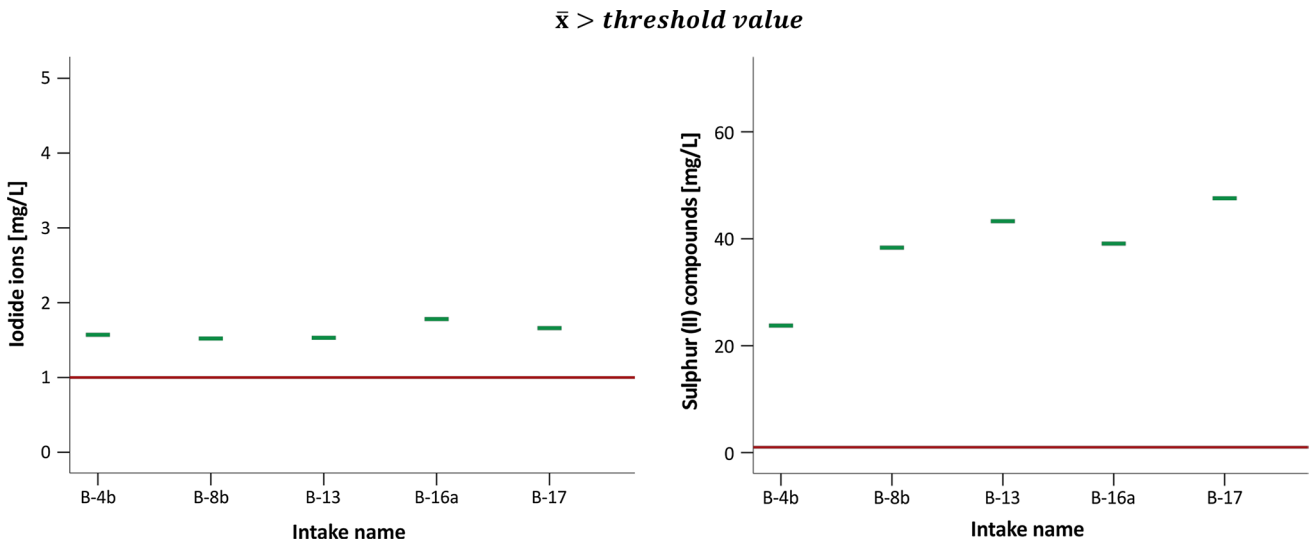

Fig. 5 Comparison of analysis results to threshold values (*red line*) for specific components in curative waters from Cretaceous level intakes, deterministic method

Table 7 Comparison of analysis results to threshold values for specific components in curative waters from Cretaceous level intakes, probabilistic method

Component	Threshold value according to RMH (2006) and GML (2011)	Decision boundary (lower limit of the variation range or uncertainty interval)	Intake name				
			B-4b Aleksander	B-8b Michał	B-13 Anna	B-16a Wiesława	B-17 Ignacy
Sulphur (II) compounds (mg/L)	1	$\bar{x} - 2\sigma$	15.97	27.89	28.76	21.94	26.19
		$\bar{x} - U_{\text{mean\_lab}}$	22.44	36.20	40.89	36.93	44.94
		$\bar{x} - U_{\text{mean}}$	23.12	37.30	42.13	38.04	46.30
Iodide ions (mg/L)	1	$\bar{x} - 2\sigma$	0.39	0	0	0	0.12
		$\bar{x} - U_{\text{mean\_lab}}$	1.47	1.42	1.43	1.66	1.54
		$\bar{x} - U_{\text{mean}}$	1.52	1.47	1.48	1.72	1.60
Hydrogeochemical type due to content of specific components for the decision limit $\bar{x} - 2\sigma$			Sulphide water	Sulphide water	Sulphide water	Sulphide water	sulphide water
Hydrogeochemical type due to content of specific components for the decision limit $\bar{x} - U_{\text{mean\_lab}}$			Sulphide and iodide water	Sulphide and iodide water	Sulphide and iodide water	Sulphide and iodide water	sulphide and iodide water
Hydrogeochemical type due to content of specific components for the decision limit $\bar{x} - U_{\text{mean}}$			Sulphide and iodide water	Sulphide and iodide water	Sulphide and iodide water	Sulphide and iodide water	sulphide and iodide water

In accordance with the guidelines provided by Ciężkowski (2007), in this case the appropriate remedial action should be taken, which involved conducting two additional analyses, 6 months apart, during 1 year. If the points continue to fall outside the set range, additional tests should be performed every quarter for 3 years. If adverse trends still be identified, the water should no longer be considered medicinal with respect to the parameter in question.

When the mean value minus the estimated uncertainty is compared to the threshold value, the variation ranges determined are above the threshold value. In this assessment variant based on the probabilistic method, the waters from the analysed intakes can be considered iodide waters.

Discussion

Based on the results of analyses of concentrations of iodide ions and sulphur (II) compounds in waters from the B-4b Aleksander, B-8b Michał, B-13 Anna, B-16a Wiesława, and B-17 Ignacy intakes, their medicinal qualities were

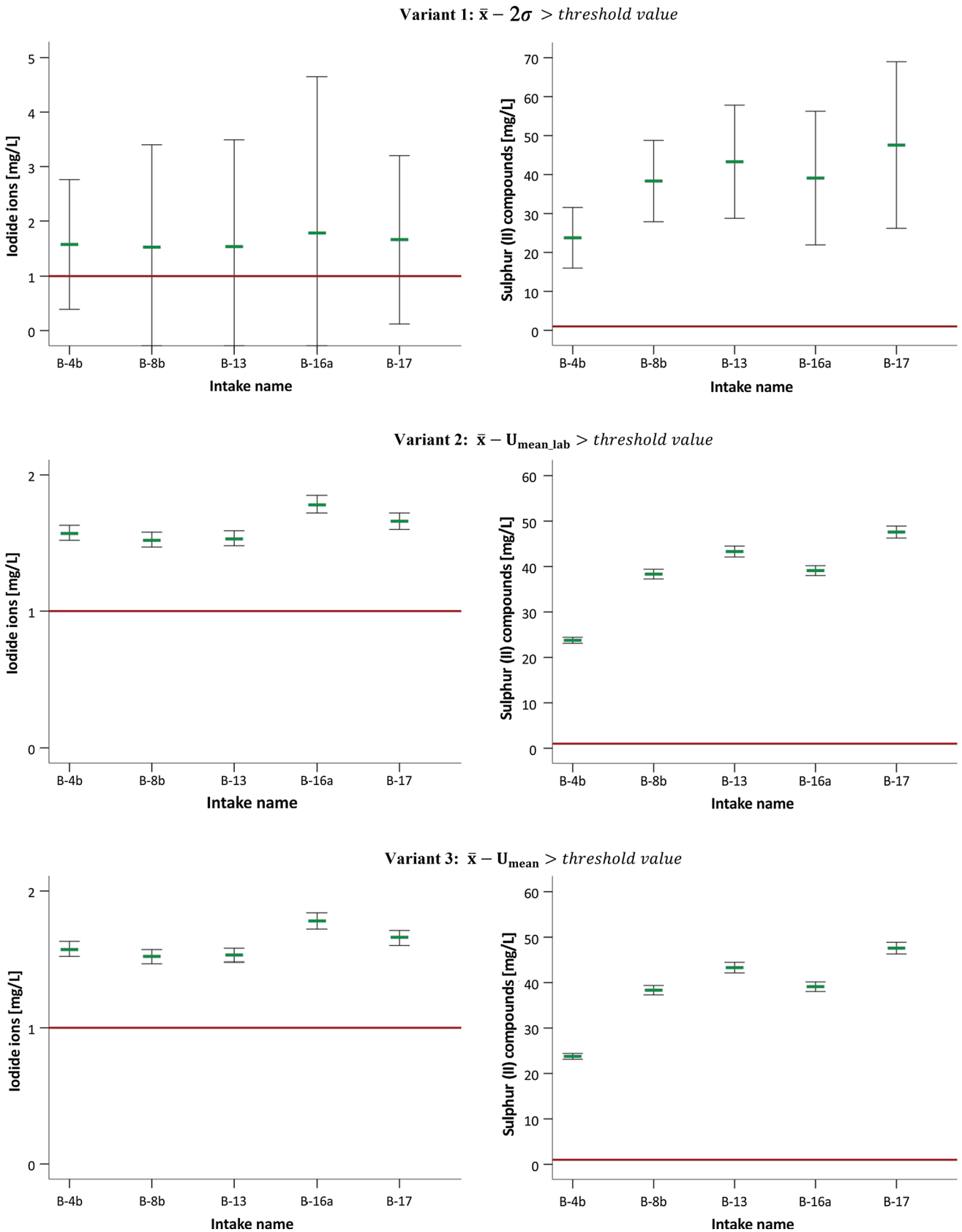

Fig. 6 Comparison of analysis results to threshold values (*red line*) for specific components in curative waters from Cretaceous level intakes, probabilistic method

evaluated using the deterministic approach and different variants of the probabilistic approach. The results obtained demonstrate significant differences between the methods used.

When the mean value for both parameters determined was directly compared against the threshold value and in the probabilistic method variants taking uncertainty into account (both laboratory uncertainty and that estimated in the ROBAN programme), it was found that the waters from the analysed intakes are sulphide-iodide waters. On the other hand, when Ciężkowski's (2007) methodology was applied, taking standard deviation into account, the threshold value for iodide ions was not reached. On this basis, the waters tested should be classified as sulphide and no iodide waters.

$\bar{x}$ - 2σ values are strongly dependent on the variation of the results of analysis over many years. For highly dispersed results in the data sets, we obtain high standard deviations and thus very low boundary decision values. This may cause the lower limit of the variation range (decision boundary) to be lower than the threshold value, even though a large majority of single measurement results are above the threshold. Standard deviation will also be greater where the natural variation of the parameter analysed is significant.

The application of the uncertainty instead of the standard deviation in the probabilistic method enables a greater number of factors that may materially affect the results of individual determinations to be taken into account. Uncertainty includes not only random effects related to the results dispersion (precision—as in the case of standard deviation) but also those resulting from the systematic errors. These effects may offset one another, resulting in smaller variation ranges than those obtained by just determining the standard deviation for the measurements. Additionally, tests of control samples carried out by a single person using the same sampling protocol and analysis procedures make it possible to minimise systematic errors to a considerable degree and reduce random errors as factors in measurement uncertainty. As a result the expanded uncertainty values determined on the basis of the analysis of duplicate samples are lower than the uncertainty declared by the laboratories and estimated during the validation of the analysis procedure.

Currently, the assessment of curative water qualities are mainly carried out by laboratories that have implemented quality control system compliant with the standard ISO/IEC 17025: 2005 (ISO 2005) and have estimated measurement uncertainties. The awareness of issues related to determination uncertainty, estimating this uncertainty in a reliable manner and then using it during the inference process, contributes to increasing the reliability of decisions concerning medicinal qualities of waters.

Conclusions

Performed analysis of medicinal qualities of water from five intakes located in Busko-Zdrój showed that there is a significant difference between results obtained using deterministic approach and different variants of the probabilistic approach. The decision about medicinal character of water is made only on the basis of the obtained result or mean value from several results. That is why the probabilistic method should be applied. However, the very important thing is to correctly define decision rules and an acceptance and a rejection zones. The use of the uncertainty allows to include not only effects associated with the results dispersion (random error as in the case when only standard deviation from multiple results is taken into account) but also some systematic errors. Furthermore, the use of the measurement uncertainty gives possibility to implement the probabilistic method in the assessing medicinal qualities of water also for an individual result.

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